

UNCLASSIFIED

MMC FILE 076

(2)

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS		
AD-A202 249		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
6a. NAME OF PERFORMING ORGANIZATION Southern Illinois University		7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office		
6b. ADDRESS (City, State, and ZIP Code) Department of Chemistry & Biochemistry Carbondale, IL 62901		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-87-K-0091		
8b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
		WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Synthesis of Laser Dyes (Unclassified)				
12. PERSONAL AUTHOR(S) John Herbert Hall				
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 5/15/87 TO 8/14/88		14. DATE OF REPORT (Year, Month, Day) 11/9/88
15. PAGE COUNT 7				
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			laser dyes, 1,3-oxazoles	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This report describes the progress made in attempts to prepare seven laser dyes. These dyes all have a 2-(4-pyridyl)-1,3-oxazole structure one dye, The synthesis of one dye, 2-(N-methyl-4-pyridinium)phenanthro[9,10-d]-1,3-oxazole tosylate (I) has been completed. Preliminary testing has shown this dye to have a quantum fluorescence yield of 0.99. It absorbs at 410 nm ($\epsilon = 2.3 \times 10^4$) and fluoresces at 534 nm in ethanol. Determination of the lifetime and output under optimum conditions is yet to be done. Work is continuing on the preparation of derivatives of I with methoxy groups on the phenanthrene ring. Three aminoketone hydrochlorides derived from 1-indanones have been prepared. These are 2-amino-1-indanone, 3,3-dimethyl-2-amino-1-indanone and 5-methoxy-3,3-dimethyl-2-amino-1-indanone. Attempts are being made to convert these into the corresponding 2-(4-pyridyl)-1,3-oxazoles.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

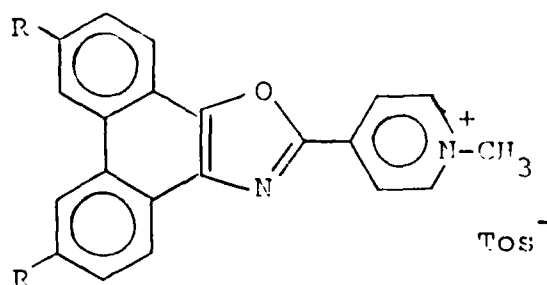
19. ABSTRACT

An attempt was made to prepare a 2-(4-pyridyl)-1,3-oxazole from the 9,10 bond of acenaphthene. The process worked, but the product condensed to form a a Diels-Alder adduct. The simple oxazole could not be isolated.

62

SYNTHESIS OF LASER DYES
FINAL REPORT

Mr. Joe Chien has succeeded in preparing laser dye Ia. He reacted phenanthraquinone with hydroxylamine to prepare a monoxime. The monoxime was reduced with hydrogen over Pd/C in methanol-HCl-H₂O solution to the aminoketone hydrochloride. The oxazole was prepared by refluxing the aminoketone hydrochloride with isonicotinic acid in phosphorous oxychloride.¹ Methylation of the oxazole with methyl p-toluenesulfonate gave dye Ia. The experimental details are in his M.S. Thesis.²

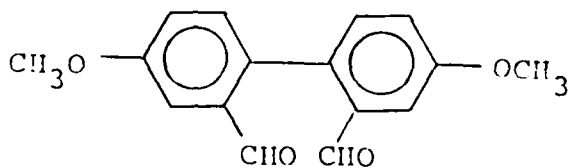


- I a. R=H
 b. R=OCH₃

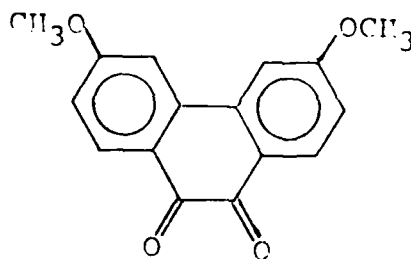
Dye Ia has been tested in methanol at MICOM in a Phase-R flash pumped laser. It had a lasing output of 9.81 ± 0.24 mJ compared to Rh-6G of 66 mJ, both at 20 KV. The threshold was 11 KV. These tests were performed in the presence of air and with no U.V. filter. These tests were not conducted under ideal conditions. Fletcher and coworkers tested a whole series of oxazole dyes and reported the best output is obtained using an argon atmosphere, aqueous alcohol as the solvent and a 1% caffeine ultraviolet filter.³ It is important that Ia be retested under these conditions. The absorption of Ia was at 410 nm ($\epsilon = 2.09 \times 10^4$) and the fluorescence spectrum was at 521 nm.

Bob Kubin at the Naval Weapons Center at China Lake, California also examined Ia. He found the absorption to be at 410 nm ($\epsilon=2.3 \times 10^4$) and the fluorescence at 534 nm in ethanol. He also found that the fluorescence quantum yield of Ia was 0.99 in ethanol.

The high fluorescence quantum yield suggests that Ia should be retested in a flash pumped laser under more ideal conditions. Further, since the introduction of methoxy groups has been shown to increase the output and increase the photostability of oxazole dyes,³ it is important that dye Ib be prepared. With this in mind, a procedure for preparing 4-methoxy-2-bromotoluene from commercially available 4-nitro-2-bromotoluene has been worked out using standard procedures. We attempted to run the Ullman reaction on 4-methoxy-2-bromotoluene using the standard procedure of heating it with copper bronze. The reaction failed. We are now approaching this problem in the following way. If 4-methoxy-2-bromotoluene can be oxidized to 4-methoxy-2-bromobenzaldehyde, it should be possible to use the so called low temperature Ullman reaction⁴ to prepare the dialdehyde II.



II



III

Ring closure of II by heating with hydrazine should give 3,6-dimethoxy-



on For

PA&I

3

sed

tion

by

Distribution/

Availability Codes

Avail and/or

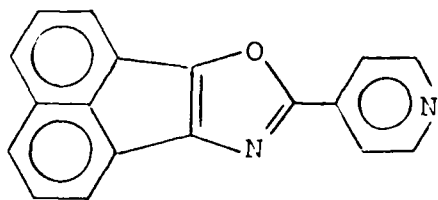
Dist

Special

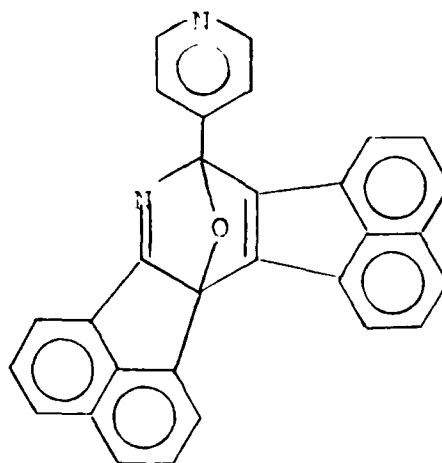
A-1

phenanthrene, which on oxidation with chromic acid should give the needed starting material, 3,6-dimethoxy-phenanthraquinone III. Conversion to Ib using the Ia procedure should be straight forward.

Joe Chien also attempted to prepare dye IV. Starting with acenaphthaquinone, the monooxime was prepared easily. Reduction over 50% Pd/C in methanol-HCl-H₂O gave the required aminoketone hydrochloride in good yield. Conversion of the aminoketone hydrochloride to the oxazole was attempted using both the one step procedure in which the aminoketone and isonicotinic acid were refluxed in phosphorus oxychloride and by the two step procedure in which the aminoketone was reacted with isonicotinoyl chloride in pyridine to give the amide, followed by refluxing of the amide in phosphorus oxychloride. Neither of these procedures gave the expected oxazole, but instead gave a compound whose structure is believed to be V, based on ¹HNMR and ¹³CNMR information.



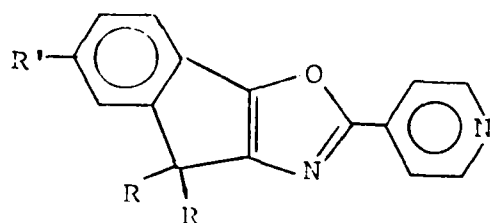
IV



V

This appears to be a Diels-Alder adduct of the expected product IV. Exactly how V is formed is not at all clear. V fluoresces only weakly and therefore has not been tested as a laser dye.

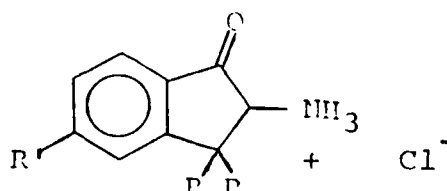
Dr. T. S. Subramanian and Dr. Hall have been attempting to prepare dyes VIa, b, and c.



VI a. $R=R'=H$

b. $R=CH_3, R'=H$

c. $R=CH_3, R'=OCH_3$



VII

The needed starting material for VIa, 1-indanone, was commercially available. The substituted 1-indanones for preparation of VIb and VIc were prepared by addition of phenylmagnesium bromide or m-methoxyphenylmagnesium bromide to ethyl isopropylidenecyanoacetate.⁵ Hydrolysis and decarboxylation in base gave 3-phenyl-3,3-dimethylpropionic acid and 3-(3-methoxyphenyl)-3,3-dimethylpropanoic acid respectively.⁶ These compounds were cyclized to 3,3-dimethyl-1-indanone and 5-methoxy-3,3-dimethyl-1-indanone by heating with polyphosphoric acid.⁷ The 1-indanones were all converted to the 2-oximes by reaction with butyl nitrite under acid conditions.⁸ Reduction of the oximes in methanol-H₂O-HCl with hydrogen over 5% Pd/C gave the hydrochlorides of the corresponding 2-amino-1-indanones (VII).

Conversion of VIIa to VIa using either the one step or two step procedures described above gave only traces of the hoped for product. When the isonicotinoyl amide of VIIa was refluxed in phosphorousoxychloride the reaction turned dark brown and then black and the only product was a black insoluble solid resembling charcoal. Shortening of the reaction time gave traces of the dye and starting material. Attempts to cyclize the amide by

refluxing in acetic anhydride gave back starting material. Heating of the amide in polyphosphoric acid or in P_2O_5 -chloroform gave an insoluble polymer. We are currently attempting to cyclize this amide using 85% phosphoric acid and acetic anhydride mixtures.

References

1. J. S. Afanasiadi, J. N. Tur and P. B. Kurapov, Chem. Heterocyclic Compounds (USSR), 397 (1985).
2. Joseph Y. Chien, "Synthesis of Oxazole Laser Dyes", M.S. Thesis Southern Illinois University, May, 1988.
3. A. N. Fletcher, R. A. Henry, M. E. Pietrak, D. E. Bliss and J. H. Hall, Appl. Phys., 43, 155 (1987).
4. Organic Synthesis, Vol. 65, p. 108.
5. A. Vogel, "Textbook of Practical Organic Chemistry", 4th ed., 1978, p. 495-496.
6. S. Winstein and R. F. Heck, J. Org. Chem., 37, 825 (1972).
7. S. Bhattachasya and D. Mukharjee, Synthetic Comm., 11(12), 993 (1981).
8. N. Levin, B. E. Graham and H. G. Kolloff, J. Org. Chem., 9, 380 (1944).

19. ABSTRACT

An attempt was made to prepare a 2-(4-pyridyl)-1,3-oxazole from the 9,10 bond of acenaphthene. The process worked, but the product condensed to form a Diels-Alder adduct. The simple oxazole could not be isolated.

6